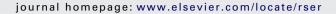


Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews





Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry

Muhammad Ayoub, Ahmad Zuhairi Abdullah*

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history: Received 22 April 2011 Received in revised form 12 January 2012 Accepted 14 January 2012 Available online 22 March 2012

Keywords: Crude glycerol Biodiesel industry Purification processes Market value Supply and demand Outlook

ABSTRACT

Biodiesel production through transesterification of vegetable oils and animal fats is rapidly increasing due to strong governmental policies and incentives. However, corresponding increase in the production of crude glycerol causes mixed effects. Sustainable biodiesel production requires optimization of its production process and drastic increase in the utilization of glycerol. High biodiesel yields and low environmental impacts, with respect to needless waste streams are mandatory. As such, upgrading of crude glycerol to highly pure glycerol and subsequent utilization of the product in producing value-added products are emerging research areas. International crude glycerol market is still at an early and very unstable stage. Globally, future conditions for an international market will largely be decided by supply and demand of glycerol for its utilization in conventional and newly developed industries. This paper highlights the current scenario on glycerol production from biodiesel industry, its global market and its new emerging outlets as commodity chemicals.

© 2012 Elsevier Ltd. All rights reserved.

Contents

1.	Introd	duction	2672
2.		erties of glycerol	
	2.1.	Characteristics of glycerol	2673
	2.2.	Glycerol formation from biodiesel production process	2673
	2.3.	Impurities in crude glycerol from biodiesel industry	2674
3.	Globa	ıl status of glycerol production	2674
	3.1.	Current glycerol production	2674
	3.2.	Projected glycerol production	2675
4.	Glyce	erol supply drivers	2676
	4.1.	Types of supply drivers involved in glycerol production	2676
	4.2.	Comparison of supply drivers for glycerol production	2676
	4.3.	Influence of supply drivers on fatty acid and soap industry	2676
5.	Globa	ıl market of crude glycerol	2677
	5.1.	Import and export	2677
	5.2.	Supply and demand	2678
6.	Impa	ct of glycerol price on biodiesel cost	2679
	6.1.	Relationship between biodiesel production cost and glycerol price	2679
	6.2.	Unstable price of glycerol	2679
	6.3.	Effect of glycerol price instability on biodiesel production cost	2680
7.	Globa	ıl utilization of glycerol	2681
	7.1.	Conventional and current glycerol usages	2681
	7.2.	Region-wise application of glycerol	2682
	7.3.	Demand-wise applications of glycerol	2682

^{*} Corresponding author. Tel.: +60 4 599 6411; fax: +60 4 594 1013. E-mail addresses: chzuhairi@eng.usm.my, azuhairi@yahoo.com (A.Z. Abdullah).

	7.4.	Outlook of biodiesel-based glycerol applications	. 2683
8.		isions	
		wledgments	
	Refere		

1. Introduction

The unexceptional opportunities have created in recent decades to replace petroleum derived materials with bio-based alternatives due to rapid depletion of fossil of fuels and its escalating prices. Petroleum is a non-regenerative source of energy and it is also an important resource of the modern society for its requirement in applications other than power like household products, clothing, agriculture, as a basic materials for synthetic materials and chemicals. Nowadays, fuel crisis has globally flounced the economy in every region, particularly the oil consuming countries due to the rapidly decreasing available global stocks. Due to this serious situation, biodiesel which comes from 100% renewable resources provides an alternative fuel option for future.

The annual biodiesel consumption in the United States was 15 billion liters in 2006. It has been growing at a rate of 30–50% per year to achieve an annual target of 30 billion liters at the end of year 2012 [1]. According to the same report by National Biodiesel Board, there were 105 biodiesel production facilities operating in the United States in 2007, and 77 other facilities were in the planning or construction stage. If all of these facilities are realized, the estimated US biodiesel production capacity will exceed 9.5 billion liters. This level of production will yield nearly 1.2 million metric tons of crude glycerol, the primary co-product of the biodiesel production process.

Purification of crude glycerol to a chemically pure substance results in a valuable industrial chemical. However, purification is costly and the glycerol market is already saturated. Thus, the price of crude glycerol continues to decline and directly affect on biodiesel production cost. This trend will continue as more biodiesel production facilities begin production. According to a report [2], the biodiesel production cost ranges from \$0.17 to \$0.42 per liter over the last decade. Today, plenty of glycerol stock is available in the world market and its price is declining day by day. The price of pure glycerol varied from \$0.50 to \$1.50/lb and crude glycerol from \$0.04/kg to \$0.33/kg over the past few years [3]. The price of glycerol in the market will continue to drop in such an over saturated market. Currently, the main supply of glycerol coming into the market is from the rapidly growing biodiesel industry.

Basically, the continuously high prices of glycerol make it worthwhile for users to be reformulated to some alternative materials such as sorbitol and synthetic glycerol. Meanwhile, sustained low prices encouraged its use in other applications. The impact of the additional huge quantity of glycerol on its prices is not clear. However, it is likely that if new uses for glycerol are not found, the glycerol price may drop to a level that even justify its use as a burner fuel, which cost is usually about 5 cents/lb. This also implies that the overproduction of low grade glycerol would impact the viability and overall economy of biodiesel production [4], market price stability of current crude glycerol as well as environmental concerns due to improper disposal of glycerol [5]. The high biofuel prices and historically low glycerol prices are two main factors that drive researchers to discover new applications of glycerol and provide an ideal platform for chemical and pharmaceutical industries.

The objective of this work is to provide a critical review on the formation and current scenario of crude glycerol resulting from biodiesel production and to provide an insight into the impact of this crude glycerol over the biodiesel production cost itself. The

study also provides a view of glycerol market and its new outlets at present and future with respect to the production of glycerol-based value-added products.

2. Properties of glycerol

Glycerol, commonly known as glycerin is a major by-product of biodiesel manufacturing process. Generally, approximately 4.53 kg of crude glycerol is created for every 45.3 kg of biodiesel produced [6]. Glycerol is a material of outstanding utility with many areas of application. A unique combination of physical and chemical properties of glycerol makes it technically versatile product which is readily compatible with many other substances and easy to handle. Glycerol is also virtually nontoxic to human health and also to environment [7]. Physically, glycerol is a water-soluble, clear, almost colorless, odorless, viscous, hygroscopic liquid with a high boiling point. Chemically, glycerol is a trihydric alcohol, capable of reacting as an alcohol, yet stable under most conditions. A list of physical and chemical properties which are important for its applications is shown in Table 1 [8]. Glycerol finds application in a broad diversity of end users.

A glycerol molecule has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Therefore, it is actually has multipurpose substance in many applications. Glycerol can be used as a renewable source for biodegradable products and also find applications in green refinery process. It may have a great environmental value demanded by modern society who favors the non-dependence on depleting sources of petroleum and fossil fuel feedstock.

Table 1Physical and chemical properties of glycerol [8].

Properties		Values
Chemical formula		CH ₂ OH-CHOH-CH ₂ OH
Formula weight		92.09
Form and color		Colorless and liquid
Specific gravity		1.260 ^{50/4}
Melting point		17.9 °C
Boiling point		290 °C
Solubility in 100 parts		
Water		Infinity
Alcohol		Infinity
Ether		Insoluble
Heat of fusion at 18.07 °C		47.49 cal/g
Viscosity of liquid glycerol		
At 100% purity		10 cP
At 50% purity		25 cP
Diffusivity in		$(DL \times 10^5 \text{ sq cm/s})$
i-Amyl alcohol		0.12
Ethanol		0.56
Water		0.94
Specific heat in	15°C (cal/g°C)	30°C (cal/g°C)
aqueous solution	(,0 ,	, ,,,
(mol%)		
2.12	0.961	0.960
4.66	0.929	0.924
11.5	0.851	0.841
43.9	0.670	0.672
100	0.555	0.576

Table 2Typical elemental analysis result of crude glycerol from biodiesel industry [9].

Elements	Weight%	Standard deviation
Carbon (C)	52.77	1.703
Hydrogen (H)	11.08	0.051
Nitrogen (N)	< 0.0001	< 0.0001
Sulfur (S)	-	_
Balance oxygen (O)	36.15	-

Table 3Ouality parameter of different categories of glycerol [11].

Parameter	Crude glycerol	Purified glycerol	Refined/ commercial glycerol ^a
Glycerol content (%) Moisture contents (%) Ash (%) Soap (%) Acidity (pH) Chloride(ppm) Color (APHA)	60–80	99.1-99.8	99.2-99.98
	1.5–6.5	0.11-0.8.	0.14-0.29
	1.5–2.5	0.054	<0.002
	3.0–5.0	0.56	N/A
	0.7–1.3	0.10-0.16	0.04-0.07
	ND	1.0	0.6-9.5
	Dark	34-45	1.8-10.3

a Ref. [12].

2.1. Characteristics of glycerol

Glycerol is a material of choice mainly because of its physical characteristics, while some other uses rely on its chemical properties. Table 2 shows the typical elemental analysis of crude glycerol generated by biodiesel industry indicating that the major elemental contents of this material are C, H, and O. The high value of the carbon content (52.77%) in glycerol make it renewable energy source for various applications while second high value of oxygen content (36.15%) suggests that it is indeed a valuable compound.

The word 'glycerin' generally applies to purified commercial products containing more than 95% of glycerol while the word 'glycerol' often specifically refers to the chemical compound of 1,2.3-propanetriol and to the anhydrous content in a glycerin product or in a formulation. Concentration is usually by weight and is normally obtained by conversion from specific gravity measurements made at either 20/20 °C or 25/25 °C [10]. In addition, glycerol can be categorized into three main types, i.e. crude glycerol, purified/refined glycerol and commercially synthesized glycerol. The major differences between these three types of glycerol from biodiesel industry can be explained by their properties as shown in Table 3. It is clear from this table that differences between purified and commercial glycerol are minor while major differences can be found between crude glycerol and purified glycerol. Actually, the purified or refined glycerol is often prepared close to the quality of commercial synthesized glycerol due to its use in sensitive materials like medicine, food and cosmetic products. It is also noted in Table 2 that crude glycerol is of 60–80% purity compared with purified or synthesis glycerol which is generally close to 100% pure [11]. Similarly, moisture, ash and soap contents are present at higher quantity in crude glycerol. The acidic value of crude glycerol is slightly higher than others and color is also dark which may due to the presence of these impurities along with some other minor impurities.

A purified or refined glycerol from crude glycerol from biodiesel industry is generally sold as 99.5–99.7% pure in the market. The common purified glycerol available in the market is manufactured to meet the requirements of the United States Pharmacopeia (USP) and the Food Chemicals Codex (FCC). However, technical grades of glycerin that are not certified as USP or FCC are also available in the market. Therefore, the quality of purified glycerol can be identified by its grade. This type of glycerol can be divided into

Table 4Commercially available basic grade of purified glycerol [13].

Grade	Type of glycerol	Preparation and usage
Grade-I	Technical grade ~99.5%	Prepared by synthetic process and used as a building block for various chemicals but not applicable to food or drug formulation
Grade-II	USP grade 96–99.5%	Prepared from animal fat or plant oil sources, suitable for food products, pharmaceuticals and cosmetics
Grade-III	Kosher or USP/FCC grade 99.5–99.7%	Prepared from plant oil sources, suitable for use in kosher foods and drinks

three basic grades on the basis of purity and potential end-uses as shown in Table 4. This table also provides the basic source of each divided glycerol category and application fields for each category of glycerol.

As a matter of fact, the cheap production of biodiesel would entail surplus glycerol production (80–88% purity) that does not meet the purity of crude glycerin of industrial grade (98% purity) [14]. Crude glycerol originating from biodiesel industry is expensive to be purified to above 99% for use in food, pharmaceuticals, or cosmetics industries. The refined glycerol market looks strong as compare to crude glycerin market and it may be due to its new feed and chemical applications.

It can be concluded that in the current scenario of glycerol market, there are different types of glycerol available in open market. The types of glycerol depend on the purity that will directly affect the end uses like food, pharmaceutical, cosmetics or chemical components preparation. It is also a notable point that majority of purified glycerol products are currently based on crude glycerol resulting from biodiesel production.

2.2. Glycerol formation from biodiesel production process

Traditionally, glycerol is obtained from four different processes, i.e. soap manufacture, fatty acid production, fatty ester production and microbial fermentation [15,16]. However, it can also be synthesized from propylene oxide [15]. The reactions for the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. Transesterification of triglycerides such as rapeseed, palm, soybean and sunflower oils has gained significance for the role in the manufacture of high quality biodiesel fuel [17,18]. Several other chemical and enzymatic processes to produce fatty acid methyl esters from vegetable oil are now commercially available [19].

Actually, glycerol is widely available and is rich in functionalists. Glycerol is found naturally in the form of fatty acid esters. It is also an important intermediate in the metabolism process of living organisms [15]. The most common way to produce biodiesel is to transesterify triacylglycerols in vegetable oil or animal fats with an alcohol in the presence of alkali or acid catalyst [20]. Methanol is the most commonly used alcohol for this process due to its low cost. This process involves the removal of the glycerin from vegetable oil or fat. During this process, methyl esters are separated as the desired product while glycerin is left behind as the by-product. Crude glycerol is normally generated at the rate of one mol of glycerol for every three mol of methyl esters synthesized. Approximately, it constitutes about 10 wt.% of the total product during the biofuel production [21].

Fig. 1 shows the basic formation of crude glycerol during the transesterification process [17]. Generally, 3 mol of methanol reacts in three steps with glycerides in the presence of catalyst to form methyl esters and glycerol. In first step methanol reacts with triglycerides to form diglycerides and methyl ester and then methanol reacts again with diglycerides to form monoglyrides and methyl ester. These monoglycerides then react again with

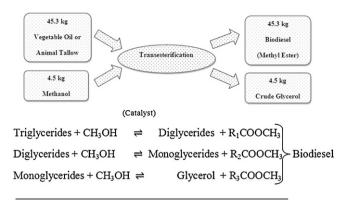


Fig. 1. Formation of crude glycerol during transesterification process [17].

methanol to form finally glycerol and methyl esters. It is also clear in the process scheme that glycerol is produced with biodiesel at a ratio of 1:10, i.e. for every 45.3 kg of biodiesel, 4.53 kg of crude glycerol is produced. Worldwide biodiesel industry's expansion is practically limited by high capital costs for glycerol refinery. The low value crude glycerol generally has 80–88% purity and needs further purification steps to meet the purity of industrial grade glycerol (99% purity).

It can be concluded that the planned massive increase in the production of biodiesel may inevitably lead to a large oversupply of crude glycerol. Some producers of synthetic glycerol have already responded to this by closing their units which may not compete under these market pressures. If the production of biodiesel continues with this trend rapidity, it might be possible that the potential annual glycerol surplus will touch its peak within the next few years.

2.3. Impurities in crude glycerol from biodiesel industry

Crude glycerol has low economic value due to the presence of various impurities. Common impurities in crude glycerol resulting from biodiesel industry are such as moisture, ash, soap and chloride contents. These impurities along with acidity and color intensity are also shown in Table 3. Sometimes, these impurities also include residual methanol especially when the alcohol is used in excess to drive chemical transesterification and total recovery of entire methanol is not achieved. On the other hand, some free fatty acids present in the initial feedstock can react with alkalis to form soaps, which are soluble in the glycerol layer.

According to a report, crude glycerol from biodiesel industry contains carbon content at an average of about 25% and a small quantity of metals like Na, Ca, K, Mg, Na, P, and S could also present. The quantities of these metals except Na usually present in the range of 4–163 ppm while sodium content could exceed 1%. Other than metals, crude glycerol from the transesterification process also contains proteins (0.06–0.44%), fats (1–13%) and carbohydrates (75–83%) [22]. It generally consists of about 65–80% glycerol. Some biodiesel plants are reported to produce crude glycerol which consists of more than 80% glycerol, depending on specific manufacturing processes. Refined glycerol has about 99.5% purity, after undergoing a highly energy intensive refining process [23]. Gonzaler-Pajuelo et al. [24] and Mu et al. [25] also reported that glycerol could made up anywhere from 65% to 85% (w/w) of the crude glycerol streams.

The process of refining glycerin involves the removal of residual non-glycerol organic matters, water, salt and odors and the operation can directly affect the cost of refined form. Then, this refined glycerin obtained from crude glycerol is used by many industries, including food, cosmetic and pharmaceutical industries. The remaining weight in the crude glycerol streams is mainly due to methanol and soap [26]. Glycerol purity value may depend upon its purification methods used by its processers and different initial feed stocks used in the biodiesel production. Thompson and He [22] reported that mustard seed feed stocks had a low purity level of glycerol (62%), soy oil feed stock had slightly high purity of glycerol (67.8%) while waste vegetable had high level of glycerol purity (76.6%). Simple reason for this difference may be due to different concentrations of elements present in crude glycerol.

Consequently, if glycerol is used for the formation of consumer products like food or drug, it must be refined well beyond the purity at which it comes out of a biodiesel plant. For crude glycerol, it might be easier to be directly used for chemical component preparation rather than for food or drugs preparation that require high purity. Therefore, the present work is mostly concerned with biodiesel based crude glycerol originating from biodiesel industry and its importance for upgrading into higher-value compounds, thereby allowing the biodiesel production to become more cost-effective. Hence, much emphasis is given on the importance of crude glycerol and conversion of this low-value by product to value-added compounds so that a better production-consumption balance can be achieved in the crude glycerol market.

3. Global status of glycerol production

The biodiesel production is increasing worldwide in recent years because of its environmental benefits and the fact that it is made from renewable biological sources [27,28]. This is the basic reason for increasing quantity of glycerol in the market. Crude glycerol was also obtained as by-product from soap and fatty acid production in past years. Currently, most of glycerol is produced from biodiesel production process. Therefore, the price of glycerol is determined by the demand and production of biodiesel instead of soap and fatty acid.

3.1. Current glycerol production

Biodiesel industry continuously produces huge amount of crude glycerol as a co-product. It is predicted that if the production of biodiesel is sustained at the same pace in future, glycerol may create handling problem for industrialists. Therefore, responsible authorities in biodiesel producing countries should take necessary proactive actions to stop subsidies for its production in order to reduce the surfeit of crude glycerol.

The glycerol production worldwide remained relatively stable and very low level from the late 1990s to 2003. Then biodiesel production slightly increased to bring about corresponding increase in the quantity of crude glycerol in 2004. After that, biodiesel production drastically increased with corresponding huge production of crude glycerin. Fig. 2 clearly shows the increasing trend of crude glycerol production due to increasing production of biodiesel during the period of 2004–2006 [29]. It is clear from the figure that glycerol production increased by an approximately a factor of four times from 62 million lbs to 213 million lbs in a mere 1 year from 2005 to 2006. The increasing quantity of glycerol was obviously due to high production of biodiesel from 75 gallons to 250 gallons during 2005–2006.

The National Biodiesel Board [30] reported an annual production of 450 million gallons of biodiesel in 2007, which was a sharp increase from less than 100 million gallons in 2005. The production of crude glycerol was very low until 2005. Basically, glycerol was produced at under 0.5 billion pounds by European Nations only

^{*} Where R₁, R₂, R₃ are hydrocarbon chain containing 15 to 21 carbon atoms

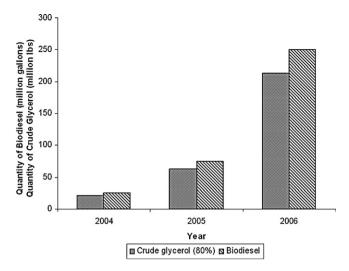


Fig. 2. Production of biodiesel and crude glycerol during 2004-2006 [29].

before 2006. After that, some other countries like USA, Malaysia, Indonesia, India and China that were involved in the production of biodiesel during 2006–2007 sharply increased the production of crude glycerol. After 2007, the production of crude glycerol rapidly increased due to huge production of biodiesel by all these countries. In addition, the federal government of Canada aims to produce 500 million liter/year of biodiesel by the year 2010 to meet the Kyoto protocol [31]. According to the BBI International's Engineering and Consulting team [32], biodiesel manufacturers created 187,000 tons of crude glycerin in 2007. In addition, there was a great slump in imports of US crude glycerol during the recent years of 2008 and 2009.

The overall crude glycerol market in the United State was depressed in these years. This was due to Southeast Asia and Europe, which were exporting glycerin to the United States in large volume and at low cost. This was a direct consequence of an

increase in the biodiesel production in Southeast Asia and Europe. At the same time, the glycerol market also experienced a drop in its demand in Asian market due to a new Argentine biodiesel market that was established in this zone.

3.2. Projected glycerol production

Actually, glycerin market is comparatively small on a global basis. Current global production of glycerin is about two billion pounds and is valued at one billion dollar annually [33]. The main regions where crude glycerol is produced in bulk are the European Union, the United States and South East Asian countries. Obviously, the glycerol market is worldwide and vulnerable to shocks in international market even though it is just a small market. Presently, new renewable fuels policies are going to be implemented in developed and developing regions like European Union, United States, South East Asia, Canada and South America. Successful implementation of the policies will ensure that the glycerol market will increase well [34]. The United States and European Union currently dominate the biodiesel and glycerol markets. However, significant growth is underway in South East Asia and China, Furthermore, the United States has a relative advantage over the EU due to the difference in exchange rates.

Fig. 3 shows the clear estimated crude glycerol production resulting from biodiesel production in different countries [35]. It is clear from this figure that the estimated production of glycerol would reach 5.8 billion pounds in 2020. This is due to demand of biodiesel that is projected at 8 billion gallons in 2020. It is also clear from this figure that glycerol production was very low, i.e. less than one billion lbs before 2006 and mostly produced by the European Union. After 2006, the production of glycerol rapidly increased and many other countries like USA, Indonesia, Malaysia, China and India started to produce glycerol. The production of glycerol after 2006 was so rapid and continued so that its production reached above 2 billion lbs in 2009. The projected data suggest that the glycerol production will attain 4 billion lbs in 2015 if its production increases at the same pace. The estimated quantity will touch to 6 billion lbs

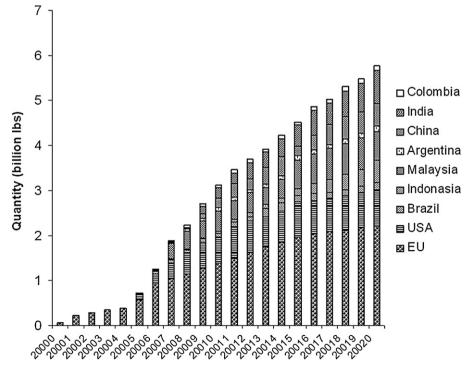


Fig. 3. Estimated production of crude glycerol in different countries [35].

Table 5 Sources of glycerol during 1992–2008 and in estimated year 2010 [37].

Glycerol sources	World glycerol production ($\times 10^3$ metric tons/year)									
	1992	1995	1999	2003	2005	2006	2008	2010		
Soaps	208	208	198	188	167	146	125	83		
Fatty acids	271	292	313	333	396	438	479	521		
Biodiesel	0	42	42	167	375	521	1125	1583		
Fatty alcohol	83	104	125	104	125	167	250	250		
Synthetic	83	83	63	63	21	0	0	0		
Others	0	0	42	63	42	0	21	21		
Total production	646	729	781	917	1125	1271	2000	2458		

after 2020. The major portion of projected glycerol quantity in 2020 belongs to EU and then USA. The other countries those will boost glycerol production in future are Malaysia, India, China, Indonesia, Brazil, Argentina and Colombia.

In Malaysia, the total combined capacity of biodiesel plants was about 1.5 million tons before 2007. In 2008, biodiesel output increased by only 5% due to the high prices of feedstock. According to a report [36], the figure is expected to show a 30% increase in 2009 as companies are cranking up their machines when the margins started to appear during the latter half of 2008. It is also mentioned in this report that another four plants with a combined capacity of 190,000 tons are going to install for a commercial production by the end of 2009. According to this data, the production of biodiesel in Malaysia may increase by more to 2 million tons at the end of 2010. Ultimately, crude glycerol production will increase in Malaysia.

Consequently, it can be concluded that the production of crude glycerol resulting from biodiesel is rapidly increasing in different religions of the world. Hence, new uses of crude glycerol are required to absorb the problem of glycerol glut in near future and researchers should study in depth to find out possible means for the utilization of glycerol in economical ways for further defraying the cost of biodiesel production.

4. Glycerol supply drivers

4.1. Types of supply drivers involved in glycerol production

An enormous change was observed between supply drivers of glycerol in the last 10 years. Changes in glycerol drivers became prominent after 2003 that saw rapid increase and overcome as a big source in 2008 and may become the strongest source in future as summarized in Table 5 [37]. It can be concluded from this table that fatty acid industry was a strong source of glycerol until year 2003. After that, the contribution of this source slowly decreased and in 2008, biodiesel became the main source of glycerol production. The reason behind this increasing trend of glycerol production was the consumption and production of biodiesel in last few years.

Another notable point in this table is that the overall production of glycerol resulting from different sources slowly increased from 646,000 MT/year to 1,271,000 MT/year during 1992–2006. The sharp increase in glycerol production was observed (2,000,000 MT/year and above) after 2006 and onwards. In addition, the production of synthetic glycerol was only observed during 1992–2005. After this period, its production became virtually zero. This is may be due to high economical production of glycerol by other sources, especially from biodiesel source.

It can be summarized that quick changes in supply drivers and production of glycerol after 2006 was attributed to biodiesel industry. The increasing quantity of crude glycerol may go to useful purpose or just a waste. It means that the utilization of glycerol in the world should increase and new uses of glycerol should be identified to open new markets of glycerol in near future.

4.2. Comparison of supply drivers for glycerol production

The source of glycerol was shifted from one of the most popular supply drivers, i.e. the fatty acids industry to biodiesel industry in past 10 years as shown in Fig. 4 [38]. It is also clear from this figure that fatty acids and soap manufacturing were two main sources for glycerol production before biodiesel industry boosted up during past few years. In 1999, the sources for production of glycerol were fatty acids, soap manufacturing process, fatty alcohols process and biodiesel process. The production ratio for these sources was at 47%, 24%, 12% and 9%, respectively. In 2009, these sources of glycerol were completely changed and they at 21%, 6%, 8% and 64%, respectively. Hence, biodiesel industry jumped up for biggest change in glycerol supply driver from 9% to 64% and fatty acid dropped from 47% to 21% during the same period.

The increasing population of the world might be a factor that urges to increase the consumption of fuel energy, i.e. increase the demand of fuel. Therefore, fuel energy is shifting from petroleum to biofuel to overcome these energy crises. Hence, biodiesel production is increasing day by day and become the biggest driver of glycerol in the last few years.

4.3. Influence of supply drivers on fatty acid and soap industry

Soap industry has conventionally provided most of the glycerin for a domestic market in developed countries like USA. Most industrialists of soap manufacturing in Europe and the Unites States have limited glycerol refining capacity. The depressed price of glycerol is another factor that prevents the construction of new refineries. Due to these problems, global crude glycerol oversupply crisis is continuously rising. Basically, biodiesel manufacturers have cut into the vegetable oil supply and driven up prices across the board and animal fats are expected to be a significant source of biodiesel in the future. Thus, natural input supplies for soap manufacturing will be

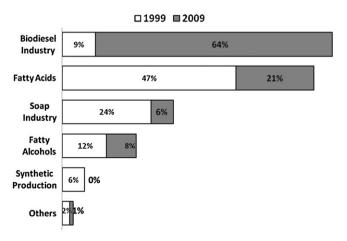


Fig. 4. Glycerol supply driver trend change [38].

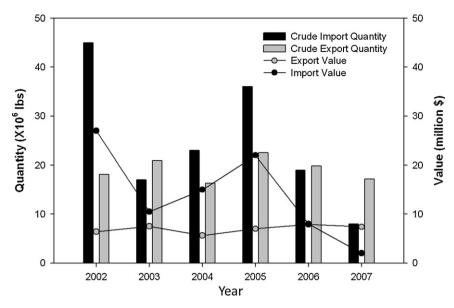


Fig. 5. The import and export of crude glycerol by USA during 2002-2007 [41].

more difficult and more expensive if biodiesel goes through major sustainable growth. Soap manufacturing industrialists are already dealing with a shortage of beef tallow. The short term remedy for soap manufacturers in the US and European countries is by importing palm oil from Malaysia or using petrochemical (synthetic) stock [39]. If these manufacturers are unable to get cheap inputs for soap manufacturing, the production will move from these countries to some other countries in foreign for cheaper labor and inputs.

Ultimately, the recent surge in biodiesel production may be alarming for soap manufacturers due to its impact on the input cost and revenue of soap manufacturing industry. According to current scenario, the dramatic increase in biodiesel production may drive up the price of fatty acid inputs and further reduce the price of glycerol in the near future. The development of some new and alternative uses of glycerol may promise the soap producers some relief from sagging glycerol prices in the future.

5. Global market of crude glycerol

According to a current scenario, it is important to know that there are two different types of glycerol markets: crude and refined. Recently, the market for crude glycerol has been relatively depressed due to a larger supply of crude than the ability to turn it into a refined product while the market for refined glycerol is still reasonably good. As the biodiesel production skyrockets, the market is being flooded with crude glycerol. The American crude glycerol supply may be distorted after a period of stable glycerol prices and a sharp fluctuation during the commodity bubble in 2008. This may cause to pull more glycerol out from already stiffening European glycerol market. It is estimated that the potential annual glycerol surplus will reach around 1.2 metric tons as targeted by the European Union and US to be achieve at the end of 2010 [35].

5.1. Import and export

As a by-product, the image of glycerin shows a poor visual image towards viability and economy of biodiesel production [40]. As fuel consumption is increasing globally day by day that has directly effected on biodiesel production and indirectly has linked with the production of crude glycerol. Fig. 5 shows the import and export quantity of crude glycerol and its value in USA during the period of

2002–2007 [41]. It is clear from this figure that import and export fluctuated over this period. The fluctuation in import was higher compare with that in export. The trend of imported crude glycerol quantity and its value fell and touched zero in 2007. However, the value of crude glycerin export was slightly stable during this period 2002–2007. Actually, after 2005, the USA biodiesel production increased, which produced enough crude glycerol. It might result in a decrease in the import of glycerol after 2005.

On the other hand, the volume of refined glycerol exports was increased during the same period which caused a decrease in the export of crude glycerol from USA. According to a European report [42], refine glycerol market is described as being strong and stable while crude glycerol market is described as week in Europe. The crude glycerin market moves at low levels due to its purity (50–90%) due to water and residual methanol contents.

Germany and Malaysia are the two largest suppliers of glycerol in the world (Table 6). It also shows the import of crude and refined glycerol by USA from these two countries (Germany and Malaysia) and rest of the world [35]. Clearly, the import of crude glycerol from Germany, Malaysia and rest of the world decreased steadily over time 2002–2007. The import of refine glycerol was seem to be stable compared with crude glycerol at the same period except from Malaysia where its import increased from 28 to 50 million kg during 2002-2004 and then decreased to 46 million kg at the end of 2007. The fluctuation in the import of crude glycerol may be due to the high shipping cost of crude glycerol from different countries to the United States. Some time shipping cost is rather high so that it does not meet the market price for crude glycerol. The import of crude glycerol from Malaysia also decreased in the same period, but it is covered by the import of refine glycerol from Malaysia during 2002-2007. It can be concluded that the overall crude glycerol import decreased but refine glycerol import increased during 2002-2007 period. Moreover, Malaysia played an important role for import of both types of glycerol during this period.

Palm oil industry of Malaysia has historically made the country a major player in the fatty acids for biodiesel production that directly influence glycerol market. It means that the country will produce more glycerol in future due to flourishing biodiesel production from palm oil. Therefore, in future, Malaysia might become the biggest exporter of crude glycerol in the world. It can also be predicted that the demand of refine glycerol may increase in future not just in the US but all over the world due to opening of new outlet of glycerol.

Table 6The imported quantity of refine and crude glycerol by USA [35].

	USA import glycerol from countries							
	Year	Germany (×10 ⁶ kg)	Malaysia (×10 ⁶ kg)	Rest of the world $(\times 10^6 \text{ kg})$	Total quantity (×10 ⁶ kg)			
	2002	14.5	24.5	6	45			
	2003	4	6	4	14			
Courds almost l	2004	9.5	1.5	12.5	23.5			
Crude glycerol	2005	1	11	24.5	36.5			
	2006	6.5	5	7.5	19			
	2007	0	3	3.5	6.5			
	2002	14	28	14	56			
	2003	14	26	20	60			
D - 6 1 1	2004	16	50	27	93			
Refine glycerol	2005	25	48	16	89			
	2006	25	37	15	77			
	2007	18	46	20	84			

It is also a notable point that refined glycerol may capture more attention in future market compare with crude glycerol due to its utilization and demand. Therefore, crude glycerol may need to be refined locally prior to its export.

5.2. Supply and demand

In previous decades, glycerol was produced as a by-product during the manufacturing or refining of several chemicals such as petroleum, soap and biodiesel. Currently supply and demand of glycerol totally change due to the shifting of supply derivers from soap and fatty acids to mostly biodiesel process. The glycerol prices can adjust to dealing with the global supply. According to previously published reports [29,43], crude glycerol prices dropped from 25 cents/lb in 2004 to 2.5-5 cents/lb in 2006 because the U.S. demand for glycerol was not large enough for all of this excess glycerol in 2007. In another report [44], it is stated that traffic fuels should contain at least 5.75% of renewable bio-components at the end of 2010. European biodiesel demand could increase to 10 million tons yearly by the end of 2010, which will produce about 1 million tons of glycerol as a by-product, if the target of this directive is to be achieved [45]. On the other hand if the United States replaces 2% of the on-road diesel with biodiesel in a B2 policy by 2012, almost 362.872 million kg of new glycerol would be added

to the market [46]. This will badly affect the demand and supply of crude glycerol in USA as well as in the EU countries.

Fig. 6 shows the supply and demand of crude glycerol during 2009 in different regions where crude glycerol played a vital role to their economy [38]. It is clear from figure that demand was high in US, Europe and China during 2009 compared with other countries where demand of crude glycerol was not so high during this time. One reason for increasing demand may be due to increasing consumers of personal care products in these markets. Presently, China is going to become a large industry for personal care products because increasing Asian people going for cosmetics and other personal care products. It can be seen in this figure that China has high demand of glycerol after the US and Europe.

It is clear from this figure that the glycerol supply during 2009 mostly originated from Europe, ASEAN, US and Latin America. In the same year, the supply of glycerol from these countries was 4 times less than its demand in China. It might be possible that the fluctuation in demand and supply is due to development of some new industries in ASAEN regions. These new industries are mostly related to personal care, new chemicals, food products and cosmetics.

According to this scenario and viewing other factors like glycerol market value that directly involved for costing of overall biodiesel production cost, it can be concluded that biodiesel may not be economically feasible any more under these circumstances. Therefore,

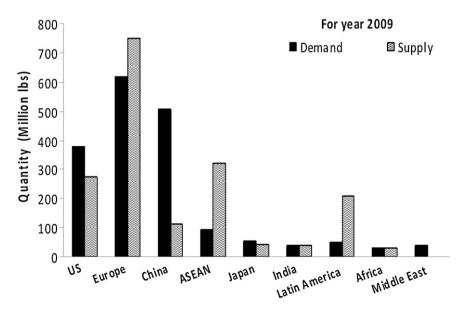


Fig. 6. Supply and demand of crude glycerol in different regions during 2009 [38].

Table 7Annual glycerol price from 2001 to 2009 [3].

Type of glycerol	Glycerol price (cent per pound)								
	2001	2002	2003	2004	2005	2006	2007	2008	2009
Synthetic	72	73	90	85	85	-	_	-	-
Refined	60	58	65	55	45	35	70.5	55	41
Crude	15	12	12	10	5	2	10	5	6

more research and technological development will be needed in future to letdown the cost of biodiesel production. Hence, utilization of glycerol in new industries on its transformation toward more value-added products with high demand may be one of the best solutions to overcome this problem.

6. Impact of glycerol price on biodiesel cost

6.1. Relationship between biodiesel production cost and glycerol price

A major obstacle in the commercialization of biodiesel is its high cost of manufacturing, particularly with respect to the raw material cost. Biodiesel usually costs over US\$0.5/L and its cost is approximately 1.5 times that of petroleum-based diesel depending upon feedstock oils [47,48]. According to Nelson et al. [49], the significant factors that affected the cost of biodiesel were feedstock cost, plant size, and value of the glycerin by-product. You et al. [9] reported that among the system variables of the plant examined, plant capacity, price of feedstock oil, and yields of glycerol and biodiesel were found to be the most significant variables affecting the economic viability of biodiesel production process. According to Zhang et al. [50], the glycerol credit could lead to approximately 13–14% reduction in total production costs of biodiesel fuel.

Consequently, it is concluded that the fluctuation in cost of oil feedstock and glycerol credit will affect the increase or decrease in the capacity of the biodiesel plants as well as production cost of biodiesel. Therefore, it can be assumed that biodiesel total production cost is directly proportional to the cost of oil feedstock and inversely proportional to glycerol credit.

6.2. Unstable price of glycerol

Currently, biodiesel production results in a rapid increase in the availability of crude glycerol worldwide and now refineries have hit the limits of their capacity. The prices for crude glycerol have fallen through the floor, falling down to zero and even negative as producers of glycerol (especially biodiesel) are forced to pay to have it taken away from their plants and incinerated [51]. On the other hand, the prices for refined glycerol have not varied inversely with biodiesel production, as might be expected. Instead, prices halved between 2003 and 2006, while growing by 69% between July 2007 and July 2008 due to other exogenous factors such as its demand in ASEAN [52]. From the 1970s until the last few years, high purity natural glycerol had a fairly stable price from about \$1200 per ton to \$1800 per ton [51]. This was based on stable markets and production. In 2000 onwards, the glycerol market became tight due to increasing production of crude glycerol. This oversupply of glycerol has significantly affected its price. Table 7 shows the price of different glycerol categories from 2001 to 2009 [3]. It is clear from this table that there is a decreasing trend in refined and crude glycerol prices during 2001–2007. In 2007, the price of both type of glycerol was found to increase to very high levels only to witness significant decreases in the following years.

The price trends of different types of glycerol during 2005–2009 are shown with better detail in Fig. 7 [38]. It can be seen that price trends of all type of glycerol even refine glycerol decreased from 2005 to first quarter of 2007. Then an increase was noted in the middle of year 2007 that continued at the end of 2007. These prices of glycerol were skyrocketing at the start of year 2008. After that prices started to decline sharply till the end of year 2008 and then again became stable at their lowest prices in year 2009. The reason

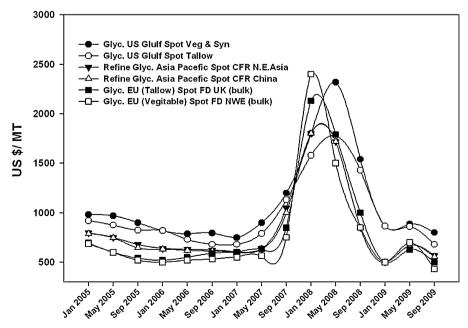


Fig. 7. The price trend of different types of glycerol during 2005–2009 [38].

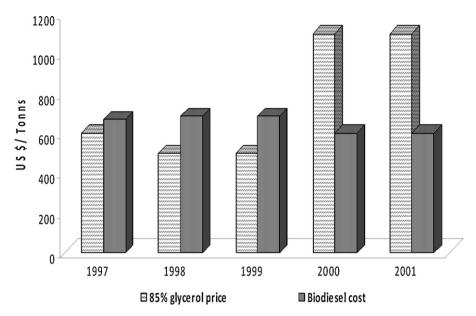


Fig. 8. Impact of glycerol price on the cost of biodiesel fuel during 1997-2001 [50].

behind increasing these prices of glycerol during 2007–2008 was the glycerol supply that began to decline rapidly during 2007–2008. The glycerol supply was disturbed due to escalating prices of seed oils during that period which directly affected the prices of glycerol [3].

According to Erik Groen's report on glycerol price in Europe [53], it is possible that glycerol price might increase in near future after start up of renewable propylene glycol (PG) plant by Archer Daniels Midland Company. It will potentially take 125,000 tons/year out of the crude glycerin market. The tighter market will increase prices even more.

It is concluded that fluctuation in glycerol pricing is due to oversupply of glycerol resulting from biodiesel production process. The fluctuation in price of glycerol from 1995 to 2006 may primarily be attributed to the slowly increasing production of biodiesel. The increasing price of glycerol during 2007–2008 was due to an imbalance between supply and demand of glycerol in global market while the drop in prices after 2008 was due to oversupply of glycerol. This may also be caused by the global economic recession and the excess production of biodiesel in those years (Table 7).

6.3. Effect of glycerol price instability on biodiesel production cost

In the context of biodiesel market, the low value of glycerol plays a vital role because it is a major by-product in the formation of biodiesel. Previous studies [25,54,55], stated that the production cost of biodiesel was found to vary inversely and linearly with variations in the market value of glycerol. A report from WOOC (2007) [56] indicates that the price trend of glycerol was decreasing over the last decade while production of glycerol was increasing due to the increase in biodiesel production. According to Fan et al. [57], biodiesel production cost could be reduced by 25% by increasing value of crude glycerol as its feedstock.

The impact of glycerol price on biodiesel production cost during 1997–2001 is shown in Fig. 8 [50]. It is clear from this figure that biodiesel cost correlate with the glycerol market price. Although, this impact was not very high, it was considerable on the total cost of biodiesel manufacturing. This figure suggests that biodiesel manufacturing cost increased to above 600 US\$/ton during 1998–1999 due to a decrease in glycerol price from 600 to 500 USD/ton. This cost then decreased to below 600 USD/ton when glycerol market price increased to above USD 1000/ton during 2000–2001 period.

Actually, the import of glycerol increased during 2000–2001 in the United States and Europe due to increased consumption. This directly affected the price of glycerol and caused a price increasing during this period as also reported by Singhabhandhu and Tezuka [58].

The sharp increase in the price of glycerol during 2007–2008 might be due to increasing demand of glycerol for new outlook. Similarly, cost of crude glycerol can be directly correlated with biodiesel price as shown in Fig. 9 [59]. It is clear from the figure that offsets price of a biodiesel increases with increasing crude glycerol price. There is a linear correlation between glycerol price and biodiesel manufacturing cost. Actually, by opening new outlets of crude glycerol, an increase in its demand which is directly linked to the overall cost of production of biodiesel could be achieved. According to another report [60], the cost of biodiesel looked very high at the start of biodiesel production due to a formation of crude glycerol. This cost of biodiesel could decrease with increasing utilization of crude glycerol to produce value-added products.

These results indicate that the amount of produced crude glycerol as a by-product has a significant effect on the net value of the total manufacturing cost of biodiesel. This cost varies inversely with variations of glycerol price in the market. Thus, the seemingly large fluctuation in glycerol price has a considerable impact

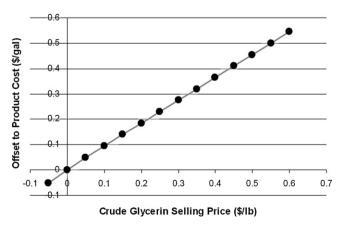


Fig. 9. Crude glycerol impact on the cost of biodiesel [59].

Table 8List of currently available and predicted outlets for crude glycerol.

Field of application	New applications of glycerol	Remarks
Chemical industry	Textile industry, plastic industry, explosives industry, polymer industry	For formation of a stain-resistant chemical and use for lubricating, sizing and softening to yarn and fabric [69] and as a substitute for petroleum-based polypropelene in a textile [70]. In the formation of nitroglycerin compound which is commonly used in all types of explosives [71]. Use as a component to produce polyglycerol ester (surfactants and lubricants), polyglycerol methacrylates (improve wood stability), polyester polyols/polyurethanes (applied as coatings, foams, and sprays) [72].
Commodity chemicals	Natural organic building blocks	For formation of natural organic building blocks [73] especially for formation of acrolein, dichloropropanol, epichlorohydrin, 1,3-propanediol, 1,2-propanediol, glycerol carbonate, DAG, MG, oxygenate fuels, glyceric acid, tartronic acid, and mesoxalic acid [74–76]. For formation of monoglyceride [77,78]. In antifogging and antistatic additives, lubricants, or plasticizers as di and tri-glycerol (polyglycerols) [79,80].
Pharmaceutical and oral care	Additive in drugs, heart disease drugs, love potion, health supplements, cosmetics, tanning agent	As an additive use in cough syrup, toothpaste, skin care, hair care medicated soap and many others drugs like expectorants, ointments, plasticizers for medicine capsules, ear infection medicines, anesthetics, lozenges, gargles, and as a carrier for antibiotics and antiseptics. Also as an ingredient in laxatives in the form of liquid enema, elixirs and expectorants [81]. Use in cosmetics for improving smoothness and as a humectant where moisturization is desired. Formation of tanning agent like dihydroxyacetone [82].
Food	Safe sweeteners, preservation, thickening agent	As a thickening agent and an ester in shortenings and margarine [83]. As an artificial sweetener, especially in low-fat foods, since it is better for blood pressure than sugar and more useful for sugar patients [84].
Livestock feed	Cow and other animals feed, pigs diet, poultry feed	Use as dairy cows feed in order to prevent ketosis [85]. As feed of pigs due to metabolizable-to-digestible energy ratio of glycerol is similar to corn or soybean oil [86] and as a feed of broiler chickens [87].
Energy as fossil fuel substitution and biogas	Liquid fuel, conversion into ethanol or hydrogen, burning as fuel pellets, combustion in incinerators, combustion as boiler fuel	Form of glycerol blend for biomass conversion to liquid fuel [88]. Trying to convert glycerol into ethanol in an anaerobic environment [89]. Aqueous phase reforming transforms glycerol into hydrogen [89,90]. Glycerol fuel pellets can use as fuel instead of coal [68]. To increase the biogas production of anaerobic digesters [70,91]. Combustion in incinerators for heat or dispose off [41]. Use as boiler fuel due to heating value is roughly 9000 BTU/lbs [61]. One ton of glycerol can be produced 600 m³ of biogas [92]. Suitable for blending agent in gasoline, biodiesel and diesel fuels [93].
Biotechnology	Organic acid, Omega-3, succinic acid by fementation, EPA by fungus	Formation of citric acid by by the yeast Yarrowia lipolytica [94], acetic acid, butyric acid and lactic acid by anaerobic fermentation [61]. Omega-3 polyunsaturated fatty acids by developing algal fermentation [95]. Eicosapentaenoic Acid (EPA) formation by the fungus Pythium irregular [26]. Feedstock in Anaerobiospirillum succiniciproducens for the production of succinic acid [96].
Miscellaneous	Basic materials, hydraulic and fire-resistant fluid, de-icing aircraft, thermo-chemical products	As a substitute for petroleum-based polypropylene, a textile, and in both rigid and flexible industrial foams [70]. It can be formulated into composites, adhesives, laminates, powder and UV-cured coatings, mouldings, novel aliphatic polyesters, co-polyesters, solvents, anti-freeze and other end uses [74,97,98]. In hydraulic fluids and fire-resistant fluids comprising glycerol-containing [99]. Use as an ingredient in products for de-icing aircraft [100]. Thermochemically conversion into propylene glycol, acetol, or a variety of other products [101,102].

on the biodiesel price. However, glycerol is indeed a valuable byproduct with much potential as a feedstock to various value-added products. As such, successful utilization for non-conventional applications could add an appreciable credit to reduce the total manufacturing cost of biodiesel fuel.

7. Global utilization of glycerol

A crude glycerol glut is created due to rapidly expanding biodiesel industry. Therefore, biodiesel producers are seeking alternative methods for its utilization or disposal. Various methods for disposal and utilization of this crude glycerol have been attempted, including combustion, composting, anaerobic digestion, animal feeds, and thermo-chemical or biological conversions to value-added products (Table 8). Crude glycerol is usually sold to large refineries for upgrading. In recent years, however, with the rapid expansion of biodiesel industry, the market is flooded with excessive crude glycerol. As a result, biodiesel producers only receive 2.5–5 cents/lb for this glycerol [61].

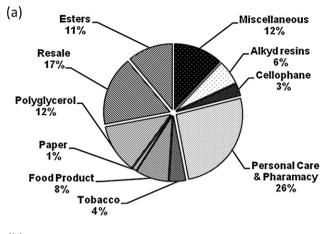
7.1. Conventional and current glycerol usages

A comparison between important applications of glycerol during 1995 [62] and 2006 [63] is shown in Fig. 10. This figure contains a complete breakdown of current and previous glycerol consumption according to its end uses. In the figure, clearly the top category

belongs to the usage in personal care and pharmaceutical industries. The demand of this category increased from 26% to 34% during 1995–2006. Actually, glycerol is an ideal ingredient in many personal care products, mostly helping to prevent moisture loss. In pharmaceuticals, it provides lubrication and smoothness to many cough syrups and elixirs.

For oral care products, glycerol is commonly found in tooth-paste, mouthwash and sugar free gum giving a sweet taste without contributing to tooth decay as well as in cosmetics to hold moisture against the skin to prevent dryness [64]. According to statistics of glycerol application in 2005, glycerol resale was the second big category (17%) as shown in Fig. 9. The resale of glycerol may decrease slowly or distributed into some other glycerol based products like increasing trend of cosmetic or may be due to development of some new outlet during that period. Therefore, there was no opportunity for resale of glycerol in 2006.

It can be seen in the figure that the usage of glycerol in paper industry is replaced by detergent production in 2006. Glycerol is also a source of carbohydrates and gives a sweet taste but it does not cause an insulin secretion during the digestion process. Glycerol is also used as humectants in food products which helps to preserve food and keep it fresh for long times. Therefore glycerol demand is increasing in food industry. According to the statistics on glycerol usages, 11% of overall glycerol was used in food industry and 6% in tobacco in 2006 compared to 8% and 4% in 2005. In the manufacturing of tobacco, glycerin is used as a humectant and



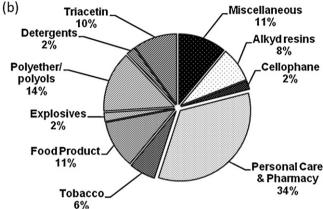


Fig. 10. Comparative end use of glycerol during (a) 1995 [62] and (b) 2006 [63].

a sweetener [65]. It is used as plastic layer in cigarette paper as well as a sweetener in chewing tobacco.

The application of glycerol as a formulation of some alkyd resins is also increasing presently. According to Fig. 10, it can be concluded that glycerol utilization in alkyd resins industry increased from 6% to 8% during these years. These materials are used as productive surface, especially in paints and components of plastics. Glycerol usage as polyether or alcoholic hydroxyl group polyol was also increased in last decade. Basically, it provides one of the basic chemical building blocks for the construction of rigid polyurethane foams. The application of glycerol as ester or triacetin remained round about same (10-11%) during 1995 and 2006. They are artificial compound which are used mostly as food additive and pharmaceutical. Another common use of crude glycerin is to burn the substance with a light temperature of (29–300 °C) for heating of industrial boilers [3]. The application of glycerol is also emerging in explosive industry. It is used for the production of nitroglycerin which is extremely powerful than TNT. Therefore, glycerol is using now as a component during explosive process and its consumption in explosive industry was noted 2% in year 2006 [63].

It can be concluded that glycerol is a non toxic element and an environmental friendly product. Therefore, its allowable quantity can be used in food, tobacco and drug manufacturing industries as a supplement is high. For large scale biodiesel producers, crude glycerol can be refined into a pure form and then it can be used in food, pharmaceutical, or cosmetics industries. For small scale producers, however, purification may too expensive to perform in their manufacturing sites. Hence, new economical applications of glycerol might be a possible solution to overcome this problem. Thus, some new glycerol based products should be added in the present market. Due to this fact, some conventional and uneconomical applications

of glycerol may disappear from upcoming market. As a result, glycerol price may rise again that will help to hail its glut resulting from biodiesel production process [62].

7.2. Region-wise application of glycerol

The important applications of glycerol are regionally determined in as shown in Fig. 11 [66]. The regional difference between the percentage of this share in three main regions, i.e. Europe, USA and Japan is shown. For the United States, the largest distinguished single application is personal and oral care products, which is above 40%. In Japan, the largest discerned single application of glycerol (25%) is for pharmaceuticals and the second largest identified application is for personal and oral care (above 15%). For the United States, the second largest application is for food and beverages (22%). Some 10% of the European glycerol market is intended for application in food and beverages with another 8% contribution for pharmaceuticals. Glycerol is used in nearly every industry. With dibasic acids such as phathalic acid, it reacts to make the important class of products known as alkyd resins, which are widely used in coating materials and paints [67]. Alkyd resins market has been increasing in the United States, Europe and Japan where it contributed about 6%, 4% and 2%, respectively. Polyether polyols have their largest share in the European market with about 12% as compared to 8% in the USA and 6% in Japan.

It can be concluded that glycerol application varies in different regions. It may be due to different culture, living style and weather of different regions. Other factors are such as the size of population, occupied area and production policies of these regions.

7.3. Demand-wise applications of glycerol

Fig. 12 illustrates the demand of crude glycerol according to its application in the different fields [37]. This figure also shows a comparative increasing percentage of crude glycerol between its traditional and new alternative uses. According to this figure, the overall increase can be seen in crude glycerol demand (above 127%) for the upcoming year (2010) as compared to that of 2005. In the projected year 2010, it is predicted that usage of glycerol may increase by 94% for new alternative applications compared with conventional application that may increase by just about 33%.

The conventional application of glycerol may increase by 18.8% in organic growth, 9% in China growth and 5.5% in additional substitution applications. For new alternative areas, most of applications are going toward feedstock/disposal and value added biochemical fields with increasing margins of 48.5% and 45.4%, respectively. The feedstock applications belong to be available for crude glycerol for feed production of animals or poultry. Meanwhile, the disposal applications will be contributed by the usage of crude glycerol for biogas production or glycerol soaked wood burn for heat purpose [68].

Presently, some US based companies such as Procter & Gamble, Cargill, Archer Daniels Midland (ADM) and Vantage Oleochemicals are refining the crude glycerol and manufacturing everything from common use toothpaste to polyols as value-added chemicals and then selling them to market [53]. It means that big and famous companies are also helping to utilize glycerol for production of value-added products. With the help of such companies, it might be possible that new alternative uses of glycerol may rise in the future.

It can be analyzed from Fig. 12 that crude glycerol demand for new alternative uses may be three times higher than its conventional applications in future. New alternatives in the future might be involved in its applications as feedstock, disposal or value added bio/chemical products. It can also be predicted that in future crude

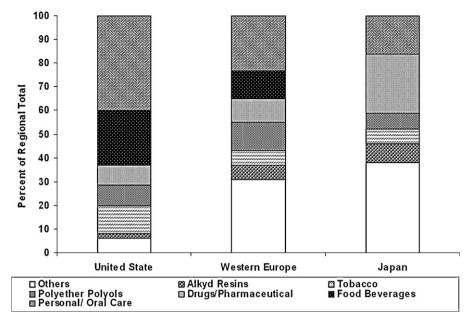


Fig. 11. Region-wise percent application of glycerol [66].

glycerol might be used in higher quantity for application of valueadded chemicals' production like glycol and epichlorohyrine.

7.4. Outlook of biodiesel-based glycerol applications

Current market is being flooded with crude glycerol due to exponentially growing production of biodiesel. Therefore, biodiesel producers are seeking some new value-added usage of crude glycerol for up coming future. The reason behind it is prohibitively cost to convert and purify crude glycerol into some conventional materials that can be used for food, cosmetics or drug industries [37,68].

There is a big range of glycerol application that starts from energy bars to cough syrups and goes through till boat coatings. According to SDA report [10], there are more than 1500 uses of glycerol. The crude glycerol derived from biodiesel production through transesterification process can be used for these applications after subjecting it to several purification processes. Actually, the purification process of crude glycerol starts with neutralization with an acid, and then water and alcohol are removed to produce 80–88% pure glycerol that is easy to be sold as crude glycerol in market. For more purification with complex operations, the glycerin is distilled to 99% or higher purity and it is sold to the cosmetic and pharmaceutical markets. Therefore, it is the necessity of present and future

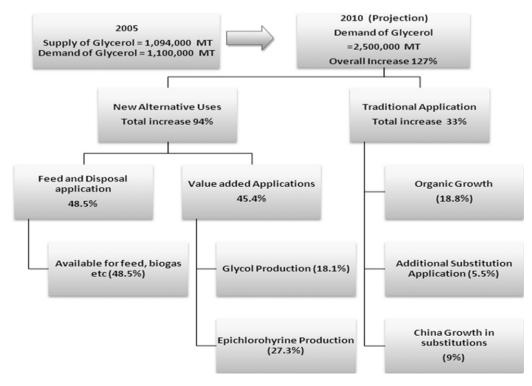


Fig. 12. Estimated demand of glycerol utilization in 2010 [68].

markets to develop some new outlets for crude glycerol resulting from biodiesel production. Equally important is the development of a more sustainable refining processes and more economical plants.

Research and development of new uses for glycerol, it is realistic hope for the industries to increase crude glycerol prices in upcoming market. The new applications may involve a large scale production after their commercial recommendation. The market of glycerol can be expected to be stable enough while at the same time the price of glycerol can rise if these huge utilizations of glycerol become successful on commercial scale. It is anticipated that the new applications of crude glycerol may strengthen the market of glycerol and indirectly support to reduce biodiesel production cost. There is still opportunity to explore more valuable applications of crude glycerol to boost up biodiesel production and to become a vital part of renewable energy.

There are several developments in various stages of the research pipeline which may add values and may provide a new outlet for glycerol industry. These developments include new application of crude glycerol as second generation biofuels, industrial chemical/biological products and livestock feed. If the new outlets for glycerol come to fruition, the price of crude glycerol may be expected to increase in future. The level of glycerol market increase depends on new value-added utilization of crude glycerol. If new outlets for glycerol, especially crude glycerol do not pan out, glycerol prices will continue to lag as experienced in past. Then, excess quantity of crude glycerol might be sold as a waste product or might be used just in incinerators to heat industrial boilers. In fact, glycerol is not a waste product but has been a staple chemical compound in the world economy for many years to come. Therefore new outlooks for glycerol industry should be continuously ventured and these might be helpful for potentially improving the economics of biodiesel production.

8. Conclusions

Glycerol is a nontoxic, biodegradable, biocompatible and versatile substrate that may be converted into numerous chemicals or bio-based products. The crude glycerol production will increase in future due to increasing consumption of biodiesel. The crude glycerol market is a complex and volatile which is mostly dependent on its global demand and supply. The demand and supply of glycerol, especially from the booming biodiesel industry, is directly correlated with its utilization and new outlets. There have been many changes in the crude glycerol market over the last two decades. For that reason, it is difficult to develop a model to predict future spot prices of crude glycerol. New applications of crude glycerol under research and development are promising, which may provide new outlets for large quantities of crude glycerol from biodiesel industry. This will help to relieve the crude glycerol glut and drive greater biodiesel production with improvement in biodiesel overall cost. The crude glycerol resulting from biodiesel production can make a handsome place in global market by using it as a source of feedstock for recovery of useful chemicals. It can be used as an additive in different fuels formulations apart from pharmaceutical and biochemical fields.

Acknowledgments

We gratefully acknowledge the support of USM Fellowship and Research Universities grant for conducting our research work on glycerol production and utilization for value-added products.

References

[1] United States Environmental Protection Agency (USEPA). EPA finalizes regulations for a renewable fuel standard (RFS) program for 2007 and beyond,

- EPA420-F-07-019. Ann Arbor, MI: Office of Transportation and Air Quality; 2007.
- [2] Higgins J. On the road to fueling the future. In: Bioenergy '02, proceedings, paper 2062. Boise, ID, September: published by Pacific Regional Biomass Energy Program; 2002.
- [3] The potential impact of rising petrochemical prices on soy use for industrial applications. Omni Tech International Ltd.; 2008. Available at: http://www.omnitechintl.com/pdf/September%202008%20Price%20Trend% 20Study.pdf [accessed on 10 January 2012].
- [4] Nitayavardhana S, Khanal SK. Biodiesel-derived crude glycerol bioconversion into animal feed: a sustainable option. Bioresour Technol 2011;10:5808–14.
- [5] Medeiros MA, Leite CMM, Lago RM. Use of glycerol by-product of biodiesel to produce an efficient dust suppressant. Chem Eng J 2012;39(1):364–9.
- [6] Cardona C, Posada J, Montoya M. Use of glycerol from biodiesel production: conversion to added value products. In: Proceedings of European Congress of Chemical Engineering (ECCE-6). 2007. p. 16–20.
- [7] U.S. Food and Drug Administration. Glycerin; GRAS status as a direct human food ingredient. Federal Register, 1979; 48(27): 5759–60.
- [8] Perry RH, Green DW, Maloney JOH. Perry's chemical engineers' handbook, 7th ed. McGraw-Hill; 1997.
- [9] You YD, Shie JL, Chang CY, Huang SH, Pai CY, Yu YH, et al. Economic cost analysis of biodiesel production: case in soybean oil. Energy Fuels 2008;22:182–9.
- [10] Glycerine an overview by Soap and Detergent Association. Available at: www.aciscience.org/docs/Glycerine-an overview.pdf [accessed on 10 January 2012].
- [11] Hazimah AH, Ooi TL, Salmiah A. Recovery of glycerol and diglycerol from glycerol pitch. J Oil Palm Res 2003;15:1–5.
- [12] Mohtar Y, Tang TS, Salmiah A. Quality of basic oleochemicals produced in Malaysia. Informatics 2001;12:529–36.
- [13] Kenkel P, Holcomb R. Feasibility of on-farm or small scale oilseed processing and biodiesel. In: English BC, Menard J, Jensen K, editors. Integration of agricultural and energy systems. Atlanta, Georgia: Global Bioenergy Partnership; 2008
- [14] Pramanik T, Tripathi S. Biodiesel clean fuel of the future. Hydrocarbon Process 2005;84(2):49–54.
- [15] Glycerol. In: Kirk-Othmer, editor. Encyclopedia of chemical technology. New York: John Wiley & Sons, Inc.; 2001.
- [16] Wang ZX, Zhuge J, Fang H, Prior BA. Glycerol production by microbial fermentation: a review. Biotechnol Adv 2001;19:201–23.
- [17] Zhou CH, Beltramini JN, Fan YX, Lu GQ. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. Chem Soc Rev 2008:37:527–49.
- [18] Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89(8):1818–25.
- [19] Wilson EK. Biodiesel revs up-fuel made from vegetable oil leads the pack of alternatives to petroleum products. Chem Eng News 2002;80:46–9.
- [20] Salamatinia B, Mootabadi H, Bhatia S, Abdullah AZ. Optimization of ultrasonicassisted heterogeneous biodiesel production from palm oil: a response surface methodology approach. Fuel Process Technol 2010;91(5):441–8.
- [21] Melero JA, Vicente G, Paniagua M, Morales G, Munoz P. Etherification of biodiesel-derived glycerol with ethanol for fuel formulation over sulfonic modified catalysts. Bioresour Technol 2012;103(1):142–51.
- [22] Thompson JC, He BB. Characterization of crude glycerol from biodiesel production from multiple feed stocks. Appl Eng Agric 2006;22(2):261–5.
- [23] Singhabhandhu A, Tezuka T. A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock. Energy 2010;35:2493-504.
- [24] Gonzalez-Pajuelo M, Meynial-Salles I, Mendes F, Andrade JC, Vasconcelos I, Soucaille P. Metabolic engineering of *Clostridium acetobutylicum* for the industrial production of 1,3-propanediol from glycerol. Metab Eng 2005;7:329–36.
- [25] Mu Y, Tend H, Zhang D, Wang W, Xiu Z. Microbial production of 1,3propanediol by Klebsiella pneumoniae using crude glycerol from biodiesel preparations. Biotechnol Lett 2006;28:1755–9.
- [26] Athalye SK, Garcua RA, Wen Z. Use of biodiesel-derived crude glycerol for producing eicosa pentaenoic acid (EPA) by the fungus *Pythium irregulare*. J Agric Food Chem 2009;57:2739–44.
- [27] Abdullah AZ, Razali N, Lee KT. Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology. Fuel Process Technol 2009;90(7–8):958–64.
- [28] Xie W, Peng H, Chen L. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. Appl Catal A 2006;300: 67–74.
- [29] Yazdani SS, Gonzalez R. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. Curr Opin Biotechnol 2007;18:213–9.
- [30] US biodiesel demand. Jefferson City, MO: National Biodiesel Board; 2008. Available at: http://www.biodiesel.org/pdf_files/fuelfactsheets/Production_ Graph_Slide.pdf [accessed on 10 January 2012].
- [31] Smith C. Biodiesel revolution gathering momentum; 2004. Available at: http://www.straight.com/print/3568 [accessed on 10 January 2012].
- [32] U.S. glycerine production soars in 2009. Available at: http://www.glycerinereport.com/20091911/us-glycerine-production-soars-2009 [accessed on 10 January 2012].
- [33] McCoy M. An unlikely impact: growth of biodiesel has big implications for the oleochemical industry. Chem Eng News 2005;83(8):19–20.

- [34] Biodiesel: prospect and challenges. Promar International; 2007. Available at: http://www.asasea.com/download.doc.php [accessed on 10 January 2012].
- [35] Glycerin market analysis. ABG Inc. Company; 2007. Available at: http://www.asasea.com/download_doc.php [accessed on 10 January 2012].
- [36] Hoh R. Malaysia biofuels annual; 2009. GAIN report number: MY9026, date: 6/12/2009.
- [37] Tsobanakis P. Cargill Incorporate, presented at biofuels and feed stocks, Indonesia; 2007. Available at: http://www.cmtevents.com/eventdatas/ 070112/Pdf/070112.pdf [accessed on 10 January 2012].
- [38] Bogaart V. Glycerin Marke Brief, Croda Oleochemicals new ideas in natural ingredients; 2009. Available at: http://www.npt.nl/vereniging/images/ stories/Verslagen/Presentatie_Bogaart_Croda_15042010.pdf [accessed on 10 January 2012].
- [39] Biofuel News. The grass farmer. Available at: http://wincustomersusa.com/ stockman/index.php?option=com_content&task=view&id=84&Itemid=9 [accessed on 10 January 2012].
- [40] Lines S. An exploding market? Utilizing waste glycerol from the biodiesel production process; 2009. Available at: http://snrecmitigation.wordpress. com/2009/04/19/an-exploding-market-utilizing-waste-glycerol-from-thebiodiesel-production-process [accessed on 10 January 2012].
- [41] U.S. Census Bureau Foreign Trade Data Dissemination. Available at: http://www.asasea.com/download.doc.php [accessed on 10 January 2012].
- [42] Kotrba R. The glycerin spread. Biodiesel Magazine, September 2007. Available at: http://www.biodieselmagazine.com/article.jsp?article_id=1797 [accessed on 10 January 2012].
- [43] Johnson DT, Taconi KA. The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. Environ Progress 2007;26:338–48.
- [44] The promotion of the use of bio-fuels or related other renewable fuels for transport. EU Directive 2003/30/EC of the European parliament and of the council; 8 May 2003.
- [45] Biofuels for transport. An international perspective. Paris, France: International Energy Agency; 2004. p. 169.
- [46] Tyson KS, Bozell J, Wallace R, Petersen E, Moens L. Biomass oil analysis, research needs and recommendations, vol. 3; 2004. NREL/TP-510-34796, pp. 74–75.
- [47] Ju YH, Vali SR. Rice bran oil as a potential source for biodiesel: a review. J Sci Ind Res 2005;64:866–82.
- [48] Ahouissoussi NBC, WetzsteiProkop ME. A comparative cost analysis of biodiesel, compressed natural gas, methanol, and diesel for transit bus systems. Available at: http://nationalbiodieselboard.com/resources/ reportsdatabase/reports/tra/19940101_tra-030.pdf [accessed on 10 January 2012].
- [49] Nelson RG, Hower SA, Weber JA. Potential feedstock supply and costs for biodiesel production. In: Bioenergy 1994, Proceedings of the sixth national bioenergy conference.
- [50] Zhang Y, Dub MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: economic assessment and sensitivity analysis. Bioresour Technol 2003:90:229–40.
- [51] Miller K. Impact of biodiesel production on the glycerol market; 2006. Available at: http://www.ruralsementes.com.br/productos/Impact. of_Biodiesel_Production_on_the_Glycerol_Market.pdf [accessed on 10 January 2012].
- [52] Gunstone FD, Hemin MPD. Glycerol an important product of the oleochemical industry. Lip Technol 2004;16(8):177–9.
- [53] Groen E. Glycerine US market runs dry prices in Europe will rise sharply. E-Energy Market; 2010. Available at: http://www.e-energymarket. com/news/link//d8e4c7fb35/browse/4/select_category/359.html [accessed on 10 January 2012].
- [54] Chiu CW, Dasari MA, Sutterlin WR, Suppes G. J Ind Eng Chem Res 2006;45:791-5.
- [55] Haas MJ. The interplay between feedstock quality and esterification technology in biodiesel production. Lip Technol 2004;16:7–11.
- [56] Woo C. Clean fuel trends in Asia: contribution of MTBE. Hydrocarbon Process 2007:86:85–8.
- [57] Fan X, Burto R. Recent development of biodiesel feedstocks and the applications of glycerol: a review. Open Fuels Energy Sci J 2009;2: 100-9.
- [58] Valliyappan T, Bakhshi NN, Dala AK. Pyrolysis of glycerol for the production of hydrogen or syn gas. Bioresour Technol 2008;99:4476–5448.
- [59] Tim M. Production and utilization. Liberty Process Technologies; 2006. Available at: http://www.xcelenergy.com/SiteCollectionDocuments/../UM-Milestone3Report.pdf [accessed on 10 January 2012].
- [60] Bozell JJ.Oleochemicals in the biorefinery: glycerol and co-products from biodiesel production 2008 transition to a bioeconomy integration of agricultural and energy systems. 2008.
- [61] Duane TJ, Katherine AT. The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. Environ Progress 2007:26:338–48.
- [62] Bondioli P. From oilseeds to industrial products: present and near future of oleochemistry. Italian J Agron 2003;7:129–35.
- [63] Pagliaro M, Rossi M. The future of glycerol. New usages for a versatile raw material. RSC Green Chem Book Ser 2008;5:212–8.
- [64] Neumann WHC. Glycerin and its history. In: Jungermann E, Sonntag NOV, editors. Cosmetic science and technology series 11. New York: Marcel Dekker, Inc.; 1991. p. 7–14 (Chapter 2).

- [65] Food ingredients. Acme-Hardesty Oleochemicals; 2010. Available at: http://www.acme-hardesty.com/product_categories/flavor%20 &%20fragrance [accessed on 10 January 2012].
- [66] SRI Consulting. Chemical economics handbook; 2006. Available at: http://www.ingenia.nl [accessed on 10 January 2012].
- [67] Moore CG. Oil modification of alkyd resins for protective coatings. JAOCS 1946;23(3):69–70.
- [68] Brady S, Tam K, Leung G, Salam Ch. Zero waste biodiesel: using glycerin and biomass to create renewable energy. UGRJ 2007;2:1–11. Available at: http://www.ugrj.ucr.edu/journal/volume2/SeanBrady.pdf [accessed on 10 lanuary 2012].
- [69] Gong CS, Du JX, Cao NJ, Tsao GT. Coproduction of ethanol and glycerol. Appl Biochem Biotechnol 2000;84–86(1–9):543–59.
- [70] Rosa DS, Bardi MAG, Machado LDB, Dias DB, Silva LGA, Kodama Y. Starch plasticized with glycerol from biodiesel and polypropylene blends: mechanical and thermal properties. J Therm Anal Calorimetry 2010;181–6.
- [71] Villamagna F, Hall BD. Explosive compositions containing glycerin, IPC8 Class: AC06B3128FI, USPC Class: 149-2; 2008. Available at: http://www.faqs.org/patents/app/20080245450 [accessed on 10 January 2012]
- [72] Pagliario M. From glycerol to value added product. Angew Chem Int Ed 2007;46:4434–40.
- [73] Cardona C, Posada J, Montoya M. Use of glycerol from biodiesel production: conversion to added value products. In: Proceedings of European Congress of Chemical Engineering (ECCE-6); 2007.
- [74] Wang K, Hawley MC, De Athos SJ. Conversion of glycerol to 1,3-propanediol via selective dehydroxylation. Ind Eng Chem Res 2003;42:2913–23.
- [75] Jerome F, Pouilloux Y, Barrault J. Rational design of solid catalysts for the selective use of glycerol as a natural organic building block. Chem Sus Chem 2008:1:586-613
- [76] Zheng Y, Chen X, Shen Y. Commoity chemicals derived from glycerol, an important biorefinery feedstock. Chem Rev 2008;108(12):5253-77.
- [77] Wibowo TY, Abdullah AZ, Zakaria R. Organo-montmorillonites as catalysts for selective synthesis of glycerol monolaurate. Appl Clay Sci 2010;50: 280-1
- [78] Hermida L, Abdullah AZ, Mohammad AR. Post-synthetically functionalized SBA-15 with organosulfonic acid and sulfated zirconia for esterification of glycerol to monoglyceride. J Appl Sci 2010;10(24):3199–206.
- [79] Clacens JM, Pouilloux Y, Barrault J. Synthesis and modification of basic mesoporous materials for the selective etherification of glycerol. Stud Surf Sci Catal 2002;143:687–95.
- [80] Martin A, Richter M. Oligomerization of glycerol a critical review. Eur J Lip Sci Technol 2010;56:456–60.
- [81] Stella M. Glycerol the sweetener that doesn't sweeten your life. Available at: http://www.diethealthclub.com/articles/500/diet-and-wellness/glycerol-the-sweetener-that-doesn-t-sweeten-your-life.html [accessed on 10 January 2012].
- [82] Bauer R, Katsikis N, Varga S, Hekmat D. Study of the inhibitory effect of the product dihydroxyacetone on *Gluconobacter oxydans* in a semi-continuous two-stage repeated-fed-batch process. Bioproc Biosyst Eng 2005;28: 37-43.
- [83] Irieb. Vegetable glycerin; 2009. Available at: http://www.vaporden.com/ notes/Vegetable.Glycerin [accessed on 10 January 2012].
- [84] Lee T, Johnson W, Earl R. May non-nutritive sweetened beverages with glycerine PCS Class: AA23L238FI, USPC Class: 426590; 2008. Available at: http://www.faqs.org/patents/app/20080226795 [accessed on 10 January 2012]
- [85] Defrain JM, Hippen AR, Kalscheur KF, Jardon PW. Feeding glycerol to transition dairy cows: effects on blood metabolites and lactation performance. J Dairy Sci 2004:87:4195–206.
- [86] Lammers PJ, Kerr BJ, Weber TE, Dozier WA, Kidd MT, Bregendahl K, et al. Digestible and metabolizable energy of crude glycerol for growing pigs. J Anim Sci 2008;86(3):602–8.
- [87] Cerrate S, Yan F, Wang Z, Coto C, Sacakli P, Waldroup PW. Evaluation of glycerine from biodiesel production as a feed ingredient for broilers. Int J Poult Sci 2006;5(11):1001-7.
- [88] Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Convers Manage 2002;43:2349–56.
- [89] Ito T, Nakashimada Y, Koichiro S, Matsui T, Nishio N. Hydrogen and ethanol production from glycerol-containing wastes discharged after biodiesel manufacturing process. J Biosci Bioeng 2005;100:260–5.
- [90] Cortright RD, Davda RR, Dumesic JA. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. Nature 2002;418:964–7.
- [91] Holm-Nielsen JB, Lomborg CJ, Oleskowicz-Popiel P, Ebensen KH. On-line near infrared monitoring of glycerol-boosted anaerobic digestion processes: evaluation of process analytical technologies. Biotechnol Bioeng 2008;99:302–13.
- [92] Hoogendoorn A, Adriaans T, Van-Kasteren JMN, Jayaraj KM. Glycerine purification via biocatalysis and column adsorption for high-quality applications, report no. 0656632-R06; 2007. Available at: http://www.ingenia.nl [accessed on 10 January 2012].
- [93] Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: a critical review. Renew Sust Energy Rev 2010;14(3):987–1000.
- [94] Papanikolaou S, Aggelis G. Lipid production by Yarrowia lipolytica growing on industrial glycerol in a single-stage continuous culture. Bioresour Technol 2002;82:43–9.

- [95] Pyle DJ, Garcia RA, Wen Z. Producing docosa hexaenoic acid (DHA)-rich algae from biodiesel-derived crude glycerol: effects of impurities on DHA production and algal biomass composition. J Agric Food Chem 2008;56(11):3933–9.
- [96] Lee PC, Lee WG, Lee SY, Chang HN. Succinic acid production with reduced by-product formation in the fermentation of Anaerobiospirillum succiniciproducens using glycerol as a carbon source. Biotechnol Bioeng 2000;72(1):41–8.
- [97] Himmi EH, Bories A, Barbirato F. Nutrient requirements for glycerol conversion to 1,3-propanediol by *Clostridium butyricum*. Bioresour Technol 1999;67(2):123–8.
- [98] Xiu ZL, Song BH, Wang ZT, Sun LH, Feng EM, Zeng AP. Optimization of dissimilation of glycerol to 1,3-propanediol by *Klebsiella pneumoniae* in one- and two-stage anaerobic cultures. Biochem Eng J 2004;19(3):189–97.
- [99] Tran BL, Hamnik JM, Blubaugh SJ. Hydraulic fluids and fire-resistant fluids comprising glycerin containing by-products. USPTO patent application 20080085846, Class: 508583, ser. no. 11/420,140; 2006.
- [100] Bhattacharjee Y. The New York Times, Harnessing biology and avoiding oil for chemical goods; 2008. Available at: http://www.nytimes.com/2008/04/09/technology/techspecial/09chem.html [accessed on 10 January 2012].
- [101] Alhanash A, Kozhevnikova EF, Kozhevnikov IV. Hydrogenolysis of glycerol to propanediol over Ru:polyoxometalate bifunctional catalyst. Catal Lett 2008;120:307–11.
- [102] Chiu C, Dasari MA, Suppes GJ, Sutterlin WR. Dehydration of glycerol to acetol via catalytic reactive distillation. AIChE J 2006;52(10):3543–8.